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Efficient adsorption of As(V) on poly(acrylo-amidino ethylene amine) nanofiber membranes

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Poly(acrylo-amidino ethylene amine) (PAEA) nanofiber membranes have been synthesized by combining the electrospinning technique and subsequent chemical modification. The membranes were used to remove As(V) from aqueous solution. The adsorption kinetics, equilibrium isotherms, and pH effect were investigated in batch experiments. The Langmuir isotherm and pseudo second-order kinetic models agree well with the experimental data. The PAEA nanofibers are effective for As(V) adsorption at pH 3. Experimental results showed that the maximum adsorption capacity of the PAEA nanofibers with As(V) is 76.92 mg g^{-1}, which is much higher than that of the PAEA microfibers (27.62 mg g^{-1}). The adsorption rate of PAEA nanofibers is faster than that of PAEA microfibers due to its higher specific surface area. The PAEA nanofibers can be used as an effective adsorbent for the removal of As(V) in aqueous solution due to high adsorption capacity and short adsorption time to achieve equilibrium.

adsorption, arsenic, electrospinning, polyacrylonitrile, nanofibers

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Arsenic has been recognized for centuries as one of the most toxic pollutants in an aqueous environment [1]. Excess arsenic in drinking water has seriously impacted on human health problems, such as skin, lung, urinary bladder, liver and kidney cancers [2]. Because of its harm to human health, it is necessary to develop new adsorbents with high adsorption ability for arsenic. Up to now, various adsorbents have been reported as materials for the adsorption of arsenic, such as modified natural zeolite [3], polymer fiber [4], nanoparticles [5], and modified magnetic chitosan chelating resin [6]. The adsorption efficiency of these adsorbents depends on the functional group(s) on their surfaces, which are effective in forming complexation or electrostatic interaction with arsenic. Various functional groups have been proposed including carboxylate, hydroxyl, amide, and amino groups. Among of them, the amino group on an adsorbent has been found to be one of the most effective chelate functional groups for adsorption of arsenic from aqueous solution [7,8].

Recently, nano-scale materials are of great interest to be developed as efficient adsorbents for metal ions. Electrospinning is known to be a simple and versatile method to generate polymer or composite nanofibrous membranes. This technique involves applying a high voltage on a viscous solution to fabricate ultrathin fibers with diameters in the range of 20–2000 nm. The electrospun nanofibrous membranes show a number of interesting characteristics such as large specific surface area and favorable morphology for recovery and recycling, in comparison to conventional microfibers. Based on the above properties, the nanofiber membranes have been speculated to have high adsorption capacity. The introduction of specific functional groups onto the electrospun nanofibers was also reported for the adsorption of specific materials from aqueous solutions [9–11].

In the present study, polyacrylonitrile (PAN) nanofiber membranes were prepared by electrospinning and they were further modified to contain amine chelating groups on their surface via reaction with ethylenediamine. Characterization of the obtained nanofibers was studied by fourier-transform

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infrared spectroscopy (FT-IR), nitrogen (N_2) adsorption-desorption isotherm analysis, and scanning electron microscopy (SEM). The investigation of the adsorption of arsenate (As(V)) from aqueous solution based on poly(acryloamidino ethylene amine) (PAEA) nanofiber membranes has been demonstrated for the first time. The purpose of our study was to (1) investigate the As(V) adsorption behaviors of the PAEA nanofibers, (2) to compare the adsorption performances of the PAEA nanofibers and PAEA microfibers in the same experimental conditions, and (3) provide an efficient adsorbent for As(V) adsorption from aqueous solution.

1 Materials and methods

1.1 Materials

Polyacrylonitrile (PAN, $M_w \approx 80000$) was purchased from Beijing Chemical Company (Beijing, China). *N*,*N*-dimethylformamide (DMF) was purchased from Tianjin Chemical Company (Tianjin, China), $Na_2HAsO_4 \cdot 7H_2O$ (As(V), purity ⩾99%), was purchased from Sigma Aldrich. Ethylenediamine and aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, purity ⩾99%) were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used without further purification.

1.2 Preparation of PAEA nanofiber mambrames

PAEA nanofiber mambrames were prepared by a simple process of two steps. In the first step, the 9 wt% PAN solution was prepared by dissolving the as-received PAN microfibers in DMF under magnetic stirring for 6 h at 80°C. Then the as-prepared gel was loaded into a syringe and connected to a high-voltage power supply. An electric potential of 15 kV was applied between the orifice and the ground at a distance of 20 cm to prepare PAN nanofibers. In the second step, PAEA nanofibers were prepared by chemical modification. In this procedure, the PAN nanofibers (0.5 g), ethylenediamine (36.5 mL) and $AlCl_3 \cdot 6H_2O$ (0.2 g) were added to a 100 mL round bottom flask. The reaction was carried out at 110°C in oil bath for 3 h. After the reaction, the obtained fibers were washed with hot deionized water, suction filtered, and were dried in a vacuum oven at room temperature overnight. For comparative purposes, PAEA microfibers were also synthesized from the as-received PAN microfibers in the same above conditions.

1.3 Sample characterization

The morphology of the nanofibers was characterized by scanning electron microscopy (SEM, Shimadzu SSX-550). FT-IR spectrum were recorded on a Bruker Vevtor-22 spectrometer from 500 to 4000 cm^{-1} using powder-pressed KBr pellets at room temperature. N_2 adsorption-desorption isotherm analysis (Micromeritics ASAP2000 apparatus at 77 K). Specific surface areas were measured by the Brunauer-Emmett-Teller (BET) method. The Brookhaven ZetaPlus system was used to determine the zeta potentials (ξ). The concentrations of As(V) ions were determined using an inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima 3300DV).

1.4 Batch adsorption studies

Adsorption kinetics was studied by adding 0.015 g of adsorbent to 100 mL of arsenate solution with an initial As(V) concentration of 12 $mg\,L^{-1}$ in a flask. The measurements of As(V) concentrations were conducted in the interval of 5 to 60 min. The adsorption isotherms were performed by adding 0.015 g adsorbent to 100 mL of As(V) solution at the initial As(V) concentration varied from 0.1 to 20 $mg\,L^{-1}$. The effect of pH on adsorption of As(V) was studied by varying the pH of As(V) solution from 3 to 9. After reached the adsorption equilibrium, the suspension was filtered through a 0.45 μm filter, and the As(V) concentrations in filtered solution were analyzed by ICP-OES.

The adsorption capacity of As(V) was calculated according to the following equation:

$$q_e = \frac{(C_o - C_e)V}{m}, \quad (1)$$

where C_0 and C_e represent the initial and equilibrium As(V) concentration ($mg\ L^{-1}$), respectively, V is the volume of aqueous solution containing As(V) (L), m is the amount of adsorbents (g), and q_e is the adsorption capacity of As(V) ($mg\,g^{-1}$).

2 Results and discussion

2.1 Characterization of PAEA nanofibers

The morphologies of nanofibrous membranes are observed by SEM and the results are shown in Figure 1. It can be seen that the membranes are composed of numerous, randomly oriented nanofibers, and the pure PAN nanofibers are smooth and uniform, with diameter between 200 to 250 nm (Figure 1(a)). The average diameter of PAEA fibers is 400–500 nm (Figure 1(b)), which shows that the reaction of the pure PAN nanofibers with ethylenediamine caused the aforementioned nanofibers to be thicker without any strong influence on their overall morphology. The diameter of the PAN microfibers (Figure 1(c)) and PAEA microfibers (Figure 1(d)) is about 16 and 23 μm, respectively.

The FT-IR spectra of the pure PAN and PAEA nanofibers are shown in Figure 2(a). For pure PAN nanofibers, The peaks can be assigned as follows: 2239 cm^{-1} (C≡N stretching), 2942 cm^{-1} (C–H stretching), 1454 cm^{-1} (C–H

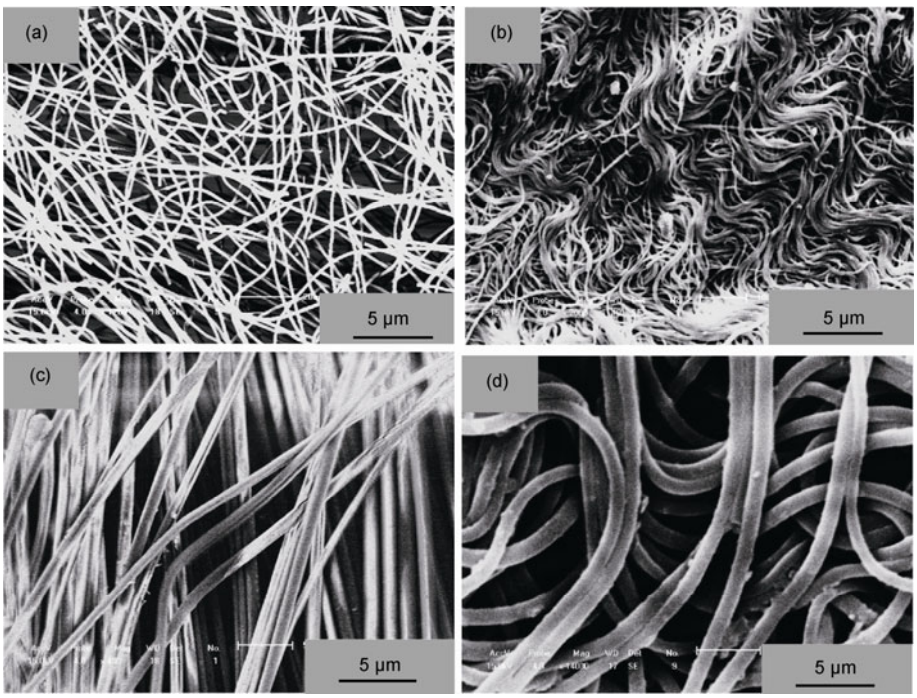


Figure 1 SEM images of the PAN nanofibers (a), PAEA nanofibers (b), PAN microfibers (c), and PAEA microfibers (d).

stretching in the backbone of the PAN fiber) [12]. After the pure PAN nanofiber is modified, new peaks at 1561 and 1654 cm^{-1} correspond to –NH bending motion combined with a –CN stretching vibration of the C(=NH)–NH– group appear and a strong broadband ranging from 3000 to 3500 cm^{-1} corresponds to the combination of the stretching vibration bands of amine (NH) group, suggesting that NH group was introduced on the surface of the PAEA nanofibers. In addition, the intensity of C≡N stretching vibration peak is reduced significantly. This shows that the reaction occurs in C≡N and results in the formation of the amidine and amine groups on the PAN nanofibers.

Figure 2(b) presents the N_2 adsorption-desorption isotherm of the PAEA nanofibers and PAEA microfibers. The shapes of the two isotherms are similar, which are the type II isotherms by IUPAC classification [13]. The type II isotherm is characteristic for nonporous adsorbents. From the isotherms, the BET specific surface area of PAEA nanofibers were 10.4 $m^2 g^{-1}$, which is higher than that of PAEA microfibers (2.8 $m^2 g^{-1}$).

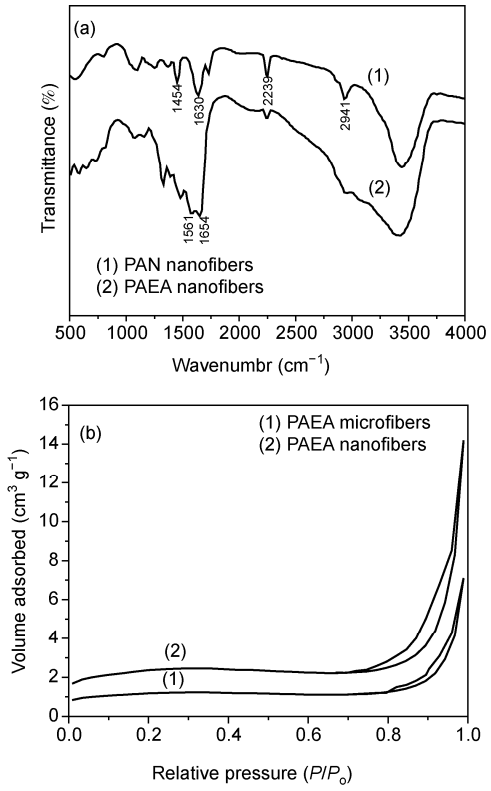


Figure 2 (a) FT-IR spectra of PAN nanofibers and PAEA nanofibers. (b) N_2 adsorption-desorption isotherms of PAEA fibers.

2.2 Adsorption kinetics

Adsorption kinetics is performed to evaluate both the equilibrium time and the rate of As(V) adsorption. The equilibrium time is one of the important parameters for subsequent adsorption isotherm studies. Figure 3 displays the effect of contacting time on the adsorption of As(V). Clearly, the adsorption of As(V) onto PAEA nanofibers and PAEA microfibers occurred rapidly and reached adsorption equilibrium after about 15 and 60 min respectively. This phenomenon can be explained by the fact that adsorption of As(V) was through the electrostatic interaction between the positive protonated amidine, amine groups and negative As(V) ions (Scheme 1) [7]. Therefore, the adsorption process

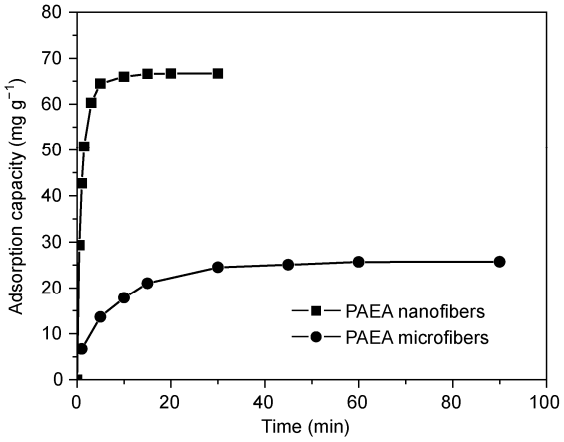


Figure 3 The effect of contacting time on the adsorption of As(V) onto PAEA fibers.

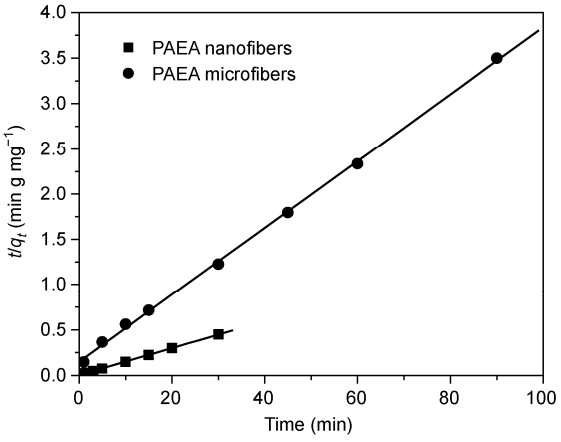


Figure 4 Pseudo second-order kinetic model plots for adsorption of As(V) onto adsorbents.

was very fast. To ensure the equilibrium adsorption of the As(V) on the adsorbents, a contact time of 120 min was chosen for subsequent adsorption isotherm studies.

To evaluate the rate of As(V) adsorption on adsorbents, the experimental data were analyzed using pseudo second-order kinetic model [14]. The pseudo second-order model has been commonly used to describe chemical adsorption process of pollutants from aqueous solutions in recent years.

The pseudo second-order adsorption kinetic rate equation is expressed in linear form as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (2)$$

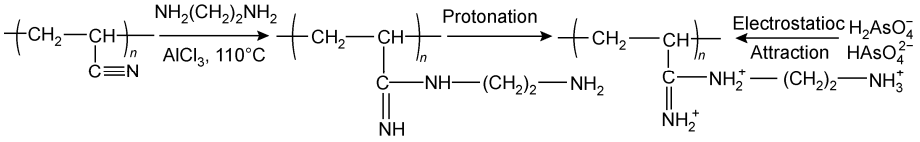
where q_e and q_t are the adsorption capacity at equilibrium and at the time t, respectively (mg g^{-1}); k_2 is the rate constant of pseudo second-order adsorption (g mg^{-1} min^{-1}), which can be determined from a plot of t/q_t versus t.

Linear regressions are frequently used to determine the best-fitting kinetic models, and the method of least squares is used for finding parameters of the kinetic model [15]. The experimental data have been analyzed by the linear methods using the OriginPro 8.0 computer software spreadsheet, and the data fits of the pseudo second-order kinetic model are shown in Figure 4. The correlation coefficient of determination, R^2, was used to test the best-fitting of the kinetic model to the experimental data.

The kinetic parameters are summarized in Table 1. The correlation coefficient (R^2) values for the pseudo second-order model (R^2: 0.9992 to 0.9998) are close to 1. Moreover, the experimental adsorption capacity (q_{exp}) values are very close to the calculated adsorption capacity (q_{cal}) values for pseudo second-order model, suggesting that the pseudo second-order kinetic model can be well-described the kinetics of As(V) adsorption onto PAEA nanofibers and PAEA microfibers. The rate constant (k_2) of PAEA nanofibers is 3.56 times than that of PAEA microfibers. Thus, the adsorption rate of PAEA nanofibers with As(V) is faster than that of PAEA microfibers, which could be related to an increase in the number of adsorption sites for PAEA nanofibers because of its higher specific surface area [16]. Consequently, the smaller diameter of the nanofibers resulted in a higher adsorption, as observed from the SEM images.

2.3 Effects of pH

The pH of the aqueous solution is an important controlling



Scheme 1 A scheme of the synthesis of PAEA and the mechanism of As(V) adsorption onto PAEA nanofibers.

Table 1 Parameters of kinetic and the isotherm for the As(V) adsorption onto adsorbents[a)]

Adsorbent	Pseudo second-order model				Langmuir isotherm model		
	$q_{e,exp}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
PAEA nanofibers	66.68	0.032	68.03	0.9998	76.92	6.19	0.9989
PAEA microfibers	25.72	0.009	27.10	0.9992	27.62	3.85	0.9980

a) $q_{e,exp}$, experimental adsorption capacity; $q_{e,cal}$, calculated adsorption capacity; k_2, the rate constant; q_m, maximum adsorption capacity; K_L, Langmuir constant.

parameter in the adsorption process. In this study, the effect of solution pH values ($3 \leqslant pH \leqslant 9$) on the adsorption amount (0.015 g of adsorbent in 100 mL of 12 mg L^{-1} As(V) and an equilibrium time of 120 min) is shown in Figure 5. At any pH value the adsorption capacity of PAEA nanofibers with As(V) is higher than that of PAEA microfibers. The adsorption capacity of As(V) onto both the PAEA nanofibers and PAEA microfibers decreases with increasing pH from 3 to 9 and reaches maximum at pH of 3. As(V) exists as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} species in aqueous solution [17]. At pH values from 3 to 6, the functions of PAEA were protonated and As(V) exists as $H_2AsO_4^-$. Thus, the As(V) adsorption onto PAEA was through the electrostatic interaction between the positive protonated amidine, amine groups and negative As(V) ions. As the pH increased, the surface of PAEA became less positive due to the deprotonation of PAEA, while the number of negative charge of As(V) increases, which causes the decrease in the adsorption capacity of the PAEA for As(V). The effect of pH can be explained by considering the surface charge on adsorbent material. The zeta potential values (ξ) were investigated to observe the surface charges of the PAEA nanofibers. The pH at which the adsorbent surface has a net neutral charge is defined as the point of zero charge (pH_{pzc}). From experimental results, the pH_{pzc} of PAEA nanofibers and PAEA microfibers were 7.6 and 7.1, respectively. When pH is lower than the point of zero charge (pzc) of the adsorbents, where PAEA surface is positively charged. Within the pH range of 3–6, As(V) exists in the $H_2AsO_4^-$. Under these conditions the adsorption of As(V) would increase due to electrostatic interaction. When pH is greater than the pH_{pzc}, where PAEA surface is negatively charged. At pH > 6, As(V) exists as $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}. Under these conditions the adsorption of As(V) would decrease due to electrostatic repulsion. To ensure quantitative adsorption, a sample pH of 3.0 was chosen as the optimum pH for further studies.

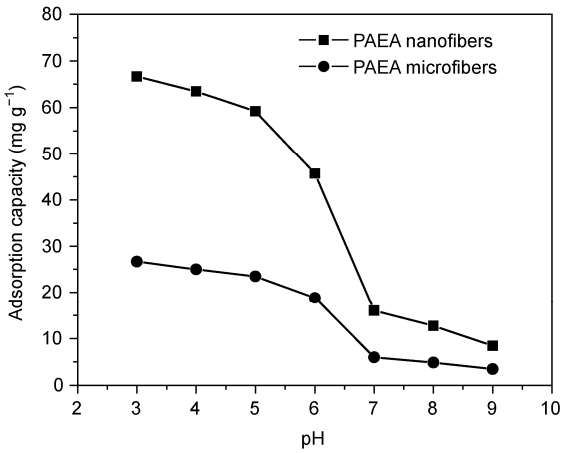


Figure 5 Effect of solution pH on the adsorption of As(V) onto PAEA fibers. In the pH range of 3–9, initial arsenic concentration 12 mg L^{-1}, T = 25°C, adsorbent dose 0.15 g L^{-1}.

2.4 Adsorption isotherm

To evaluate the As(V) maximum adsorption capacity onto adsorbents, various mathematical models can be used to analyze adsorption data. The most common one is the Langmuir model. Mathematically, the linear Langmuir isotherm equation can be written as follow [18]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}. \quad (3)$$

The values of q_m and K_L were calculated from the slope and intercept respectively from the linear plot of C_e/q_e versus C_e.

Figure 6 shows experimental data with linear equation of the Langmuir isotherm model obtained by using the linear method [19]. The slopes of the linear isotherm plots were used to calculate the parameters of the isotherm for As(V) adsorption, and the results are summarized in Table 1.

According to the obtained results, the adsorption equilibrium data of the As(V) on the adsorbents are fitted particularly well with the Langmuir model, as indicated by the very high values of the correlation coefficient ($R^2 > 0.99$). Thus, monolayer adsorption happened on the adsorbents. As shown in Table 1, the maximum adsorption capacity of As(V) on the PAEA nanofibers is 76.92 mg g^{-1}, which is higher than that of PAEA microfibers (27.62 mg g^{-1}). The maximum adsorption capacity of As(V) with PAEA nanofibers is also compared with other adsorbents, reported in the literatures [3,5,6,20] (Table 2). It can be seen that the maximum adsorption capacity of As(V) with PAEA nanofibers is higher than that with many other adsorbents, especially in small dosage and relative short equilibrium time. So it can be concluded that the PAEA nanofibers could be used as an effective adsorbent for adsorption of As(V) in aqueous solution.

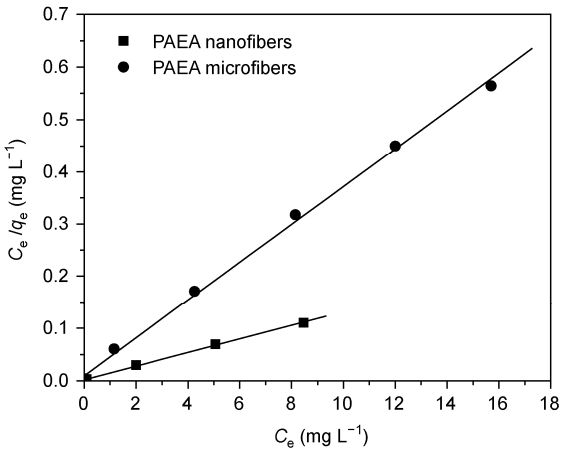


Figure 6 The plots of linear Langmuir isotherms of As(V) adsorption onto PAEA fibers. In the initial arsenic concentration range of 0.1 to 20 mg L^{-1}, pH 3.0, T = 25°C, adsorbent dose 0.15 g L^{-1}.

Table 2 Comparison of maximum adsorption capacities of various adsorbents for As(V)

Adsorbent	pH	Equilibrium time (min)	q_m (mg g^{-1})	Ref.
Modified natural zeolite	7	60	9.2×10^{-3}	[3]
Hydrous titanium dioxide	4	240	33.40	[5]
Modified magnetic chitosan chelating resin	2	120	62.42	[6]
Fe_3O_4 nanoparticle-coated boron nitride nanotubes	6.9	720	32.20	[20]
PAEA microfibers	3	60	27.62	This study
PAEA nanofibers	3	15	76.92	This study

3 Conclusions

PAN nanofiber membranes were prepared by electrospinning and they were further modified with ethylenediamine to prepare PAEA nanofibers. The PAEA nanofibers exhibit remarkably high adsorption capacity for As(V). The adsorption of As(V) onto PAEA nanofibers occurred rapidly and reached adsorption equilibrium after about 15 min. The adsorption of As(V) fits well with the Langmuir equation, and with the maximum adsorption capacity being 76.92 mg g^{-1} at 25°C. The obtained results suggest that the PAEA nanofibers possess a tremendous potential for the removal of As(V) from aqueous solution.

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